ABSTRACT OF THE DISCLOSURE

Further improvements have been made in processes for controlled polymerization of free radically (co)polymerizable monomers mediated by a transition metal complex participating in a redox reaction which involves transfer of a radically transferable atom or group to and from an initiator or dormant polymer and the growing active polymer chain ends. Two improvements involve the choice of counterion in the transition metal complex. In one improvement the transition metal is held in close conjunction with a solid support through interaction with a counterion directly attached to the support. This cognition also allows for improvements in catalyst utilization including catalyst recovery and recycle. In another improvement, particularly suitable for controlled polymerization of certain monomers with an expanded range of transition metals, the function of counterion and ligand in the development of the transition metal based catalyst is superseded by use of salt containing a soluble organic counterion. These and other process improvements have been employed to prepare an extended range of novel polymeric materials and novel processes for the preparation of functional polymers including a novel catalytic Atom Transfer Coupling Reaction.